A Report on

Investigation on structural, electronic and optical properties of thin films of Bi, Te, Sb and their binary mixtures with special reference to their topological insulator phases

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CONTENTS

- Introduction
- Review of Literature
- Research gaps
- Motivation
- Objectives
- Research Methodology
- Research Work Plan
- References

1. INTRODUCTION

1.1 Nanomaterials and their properties:

Nanoscience is the study of extremely small structures of the order of 1-100nm. It involves preparation of nanoparticles, use various techniques for their characterization and investigate their properties to understand their behaviour.

At nanoscale the materials shows properties vary different from the bulk materials. When we go from macro to micro and nano a surface area per unit volume increases. This brings about changes in the physical appearance, structural and electronic properties of the material. For example, as the size of particle decreases color of gold changes from yellow to red at about 20nm. At size of nanoscale the delivery of drugs in human beings becomes easy and more effective and it may be possible to delivery of the drug at the location of disease where it required.

The importance of nanomaterials lies in the special properties shown by them, such as high electrical conductance, chemical reactivity and magnetic effects, optical properties and physical strength as compared to bulk materials, as a result of their enhanced small size.

Nanotechnology works on matter at dimensions in the nanometer scale length (1-100 nm), and thus can be used for a broad range of applications and the creation of various types of nano materials and nano devices. A brief description of various properties of nanoparticles is given below:

1.2 Physical properties of nanoparticles

Nanoparticles are unique because of their large surface area and this dominates the contributions made by the small bulk of the material. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions.

Other examples of the physical properties of nanoparticles:

Color – Nanoparticles of yellow gold and gray silicon are red in color

Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C)

Absorption of solar radiation in photovoltaic cells is much higher in nanoparticles than it is in thin films of continuous sheets of bulk material - since the particles are smaller in size, they absorb greater amount of solar radiation because of larger surface area.

1.3 Semisolid or soft nanoparticles

Semi-solid and soft nanoparticles have been manufactured. Of these notable is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs, antibiotics and antifungal drugs and vaccines.

1.4 Optical properties of nanoparticles

Nanoparticles also often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. One example of this is that gold nanoparticles appear deep red to black in solution.

1.5 Formation of suspensions

An important physical property of nanoparticles is their ability to form suspensions. This is possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences. In bulk materials this interaction usually results in a material either sinking or floating in a liquid.

1.6 Magnetization and other properties of nanoparticles

Other properties unique among nanoparticles are quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super-paramagnetism in magnetic materials.

For example, ferroelectric materials of size smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage. Thus this property of nanoparticles is not always desirable for formation of memory devices.

1.7 Diffusion properties of nanoparticles

At elevated temperatures especially, nanoparticles possess the property of diffusion. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. Although this does not affect the density of the final product but there is a chance of agglomeration.

1.8 Hard nanoparticles

Clay nanoparticles, when incorporated into polymer matrices, increase reinforcement, leading to stronger plastics. These nanoparticles are hard, and impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibres in order to create smart and functional clothing.

1.9 Dimensionality

Nanoparticles are generally classified based on their dimensionality, morphology, composition, uniformity, and agglomeration.

1D nanomaterials

These are one dimensional in the nanometer scale viz. nano ribbon. They are typically thin films or surface coatings, and include the circuitry of computer chips and the antireflection and hard coatings on eyeglasses. These have been used in electronics, chemistry, and engineering.

2D nanomaterials

Two-dimensional nanomaterials have two dimensions in the nanometer scale. These include 2D nanostructured films, with nanostructures firmly attached to a substrate, or nanopore filters used for small particle separation and filtration. Asbestos fibers are an example of 2D nanoparticles.

3D nanomaterials

Materials that are nanoscaled in all three dimensions are considered 3D nanomaterials. These include thin films deposited under conditions that generate atomic-scale porosity, colloids, and free nanoparticles with various morphologies

Thin films

If the thickness of the material slab/film is less than 500nm, then the material is said to be thin film. Ideally it is a layer of single atom thickness deposited on any substrate and if the thickness of the film is more than 500 nm than that film is said to be the thick film. The material of large dimensions material is called the bulk material

A thin film is a very fine and thin layer of material that can be so small, ranging from fractions of a nano-meter in thickness to about 100 nm in size. Thin film applications include optical coating for a lens or mirror, and electronic semiconductor devices. Thin film application can also be used for product protection purposes. Thin film materials have been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors and light crystal displays, lithography, micro -electromechanical systems (MEMS) and multifunctional emerging coatings, as well as other emerging cutting technologies.

Different methods of preparing nanoparticles may be divided into two categories, viz;

1. Top down
2. Bottom up

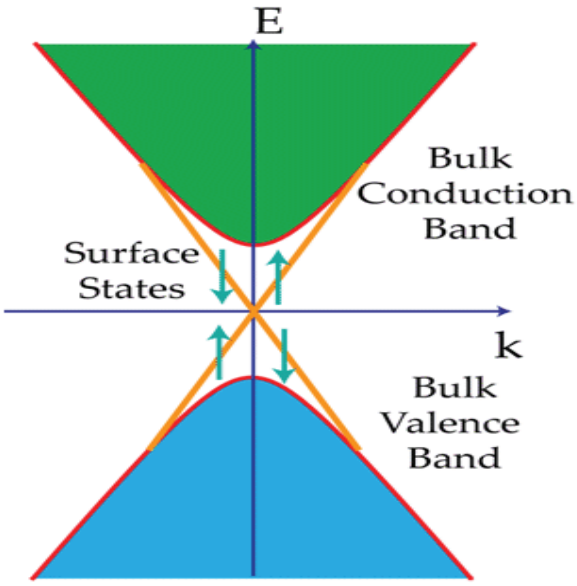
Thin film deposition methods can be further classified as either chemical or physical methods. The differences between the chemical and physical thin film deposition methods depend upon the method of depositing thin film material on the substrate.

In chemical deposition technique, fluid precursor is used which chemically reacts with the substrate. Since the thin film material is conducted through the fluid precursor, chemical deposition is conformal approaching the substrate without preference to a particular direction. A conformal is an uneven interface with the body and has a constant thickness on horizontal and vertical surfaces.

In physical deposition technique, mechanical or electromechanical methods are used to deposit the thin films on the substrate. Materials to be deposited on the substrate depend upon the temperature, pressure and other physical conditions. In the physical methods, the thin films formed are directional in nature, because the particles follow a straight path from the source to the target substrate in vacuum.

2. Topological insulators

A topological insulator is a material with non-trivial symmetry protected in topological order that behaves as an insulator in its interior but whose surface contains conducting states, meaning that electrons can move only along the surface state of the material. Recently a new class of topological states has emerged, called quantum spin hall(QSH) states or topological insulators. Examples of topological insulators are: Bi_2Te_3, Sb_2Te_3, Bi_2Se_3 etc.



Surface states of topological insulators

Some important properties of topological insulators are as given below:

One special features of topological insulators is that they show quantum Hall Effect.

The quantum spin Hall state is a state of matter proposed to exist in special, two-dimensional, semiconductors that have a quantized spin-Hall conductance and a vanishing charge-Hall conductance. The quantum spin Hall state of matter is the cousin of the integer quantum Hall state, and that does not require the application of a large magnetic field. The quantum spin Hall state does not break charge conservation symmetry and spin-conservation symmetry (in order to have well defined Hall conductances). The first proposal for the existence of a quantum spin Hall state was developed by Kane and Mele who adapted an earlier model for graphene by F. Duncan M. Haldane which exhibits an integer quantum Hall effect. The Kane and Mele model is two copies of the Haldane model such that the spin up electron exhibits a chiral integer quantum Hall Effect while the spin down electron exhibits an anti-chiral integer quantum Hall effect. Kane and Mele introduced a topological Z_2 invariant which characterizes a state as trivial or non-trivial band insulator (regardless if the state exhibits or does not exhibit a quantum spin Hall effect). Further stability studies of the edge liquid through which conduction takes place in the quantum spin Hall state proved, both analytically and numerically that the non-trivial state is robust to both interactions and extra spin-orbit coupling terms that mix spin-up and spin-down electrons. Such a non-trivial state (exhibiting or not exhibiting a quantum spin Hall effect) is called a topological insulator, which is an example of symmetry protected topological order protected by charge conservation symmetry and time reversal symmetry.

Bismuth telluride (Bi_2Te_3)

Bismuth Telluride is a grey powder with metallic luster. It is one of the best performing materials from the point of view of thermoelectric properties. It is prepared by sealing a sample of bismuth and tellurium metal in a quartz tube under vacuum and heating it to 800°c in a muffle furnace. It behave as topological insulator at 300 to 470K. Metallic single-crystal of bismuth has an extremely high magnetoresistance (where the electrical resistance is known to increase with magnetic field), giving rise to the potential for creating very good magnetic field sensors. Such metallic forms of bismuth

typically demonstrate a resistance that decreases by two orders of magnitude when cooled to liquid helium temperatures (~5 K).

2.2.2 Bismuth selenide (Bi_2Se_3)

Polyvinyl pyrrolidone (0.9 g) was dissolved in ethylene glycol (EG, 36 mL). Then bismuth oxide powder (Bi_2O_3, 1 mmol), selenium powder (Se, 3 mmol) and ethylenediamine tetraacetic acid powder (4 mmol) were added into above-mentioned EG solution. The resulting suspension was stirred vigorously and subsequently sealed in a steel autoclave. The autoclave was heated to 200°C in 30 min and maintained this temperature for 20 hours. The as-obtained product was collected by high-speed centrifugation, washed several times with deionized water and absolute ethanol, and finally dried at 60°C for 96 hours in an oven. Bismuth selenide has a threnostic platform for simultaneous cancer imaging and therapy. It shows thermoelectric and photoelectric properties. In cancer therapy due to its photothermal therapeutic capabilities, it absorb NIR laser and transfer laser energy into heat. It has low toxicity.

2.2.3 Antimony telluride (Sb_2Te_3)

Antimony telluride has thermoelectric micro refrigerator-based properties. It can be used as a buffer layer of solar cell due to its narrow band gap of 0.30 eV in semiconductor, to make low resistance ohmic contact. It can be formed by the reaction of antimony with tellurium at 500 to 900°c. It has been widely used in the industrial applications, such as target material in television camera, microwave device, switching devices, thermo electric devices and opto-selectric devices due to its attractive photoconducting properties and its high seeback coefficient, low thermal conductivity, low electrical resistivity, low band gap and long term stability. In optoelectronic devices it is used as a back contact to CdTe based solar cells, mainly because it offers long term stability and is Cu-free.

Properties of topological insulators

Types of properties	Items	Bi_2Se_3	Sb_2Te_3	Bi_2Te_3
Physical properties	Density a Lattice constant c Lattice constant	7.51 g/cc 4.14 Å 28.7 Å	6.44 g/cc 4.25 Å 30.3 Å	7.73 g/cc 4.38 Å 30.45 Å
Electrical properties	Band gap Electron mobility	0.35 eV 600 $cm^2/V.s$	0.30 eV 275 $cm^2/V.s$	0.21 eV 1140 $cm^2/V.s$
Thermal properties	Thermal conductivity Melting point	2.40 W/m.K 706 °C	1.65 W/m.K 622 °C	3.00 W/m.K 585 °C
Descriptive properties	Color Crystal structure	Black Hexagonal-rhombohedral tetradymite structure-R-(3)M	Gray Hexagonal-rhombohedral tetradymite structure-R-(3)M	Gray Hexagonal-rhombohedral tetradymite structure-R-(3)M
Optimum growth temperature		550 °C	200 °C	400 °C

3. REVIEW OF LITERATURE

3.1 Wan Lee et. al (2017) studied the "Improvement of Thermoelectric properties of Bi_2Te_3 and Sb_2Te_3 films grown on Grephene substrate". A study of substrate effect on the thermoelectric (TE) properties of Bi_2Te_3 (BT) and Sb_2Te_3(ST) thin films grown by plasma-enhanced chemical vapor deposition (PECVD) was performed. Graphene substrates which have small lattice mismatch with BT and ST were used for the preparation of highly oriented BT and ST thin films. Carrier mobility of the epitaxial BT and ST films grown on the graphene substrates increased as the deposition temperature increased, which was not observed in that of SiO_2/Si substrates. Seebeck coefficients of the as-grown BT and ST films were observed to be maintained even though carrier concentration increased in the epitaxial BT and ST films on graphene substrate. Although Seebeck coefficient was not improved, power factor of the as-grown BT and ST films was considerably enhanced due to the increase of electrical conductivity resulting from the high carrier mobility and moderate carrier concentration in the epitaxial BT and ST films.

3.2 Swati Arora et. al (2017) studied the "Properties of Nanostructure Bismuth Telluride Thin Films Using Thermal Evaporation". Bismuth telluride has high thermoelectric performance at room temperature. Several nanostructure thin films of bismuth telluride were fabricated on silicon substrates at room temperature using thermal evaporation method. Tellurium (Te) and bismuth (Bi) were deposited on silicon substrate in different ratio of thickness. These films were annealed at 50°C and 100°C. After heat treatment, the thin films attained the semiconductor nature. Samples were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to show granular growth. Thin films indicate that after annealing there are tiny gaps that have appeared between the granules which may be due to diffusion of tellurium in bismuth and also confirm their mixing after annealing. It was observed that the bismuth telluride thin films after annealing attain the semiconductor nature and show nonlinear behaviour.

3.3 Irfan et. al (2016) studied the "Characterization and synthesis of Bi_2Se_3 topological insulator thin film using thermal evaporation". Topological insulators are the new phase of matter with bulk insulating and conducting surface states. Among the known three dimensional topological insulators, bismuth selenide (Bi_2Se_3) is one of the most promising materials for studying topological insulating properties. Bi_2Se_3 thin films were grown using thermal evaporation technique and atomically smooth films were obtained by post annealing treatment. Pure phase of Bi_2Se_3 is confirmed using x-ray diffraction; Raman spectroscopy shows a strong intensity of A11g, E2g and A21g modes in Bi_2Se_3 thin films. The surface studies on these films are carried out using scanning electron microscopy and atomic force microscopy. X-ray photoelectron spectroscopy (XPS) is used for elemental analyses in Bi_2Se_3 thin film. The surface quality of the film is improved with plasma etching (i.e. argon etching) in XPS. High quality Bi_2Se_3 thin films can be used further for investigation on transport properties of topological insulators

3.4 Das et. al (2015) studied the "Electrical Properties of Thermal Evaporated Bismuth Telluride Thin Films". Bismuth Telluride films (Bi_2Te_3) were fabricated using thermal evaporation technique in a vacuum better than 10-5 torr onto glass substrate. The study of electrical properties of Bi_2Te_3 thin films was carried out in the thickness range of about 50-300 nm and temperature range 300-470K. The electrical conductivity was found to increase with thickness of the films and temperatures. The activation energy was decreased with film thickness while the grain size was increased with the thickness. The temperature co-efficient of resistance (TCR) was found to be negative that indicates its non-metallic behavior. The Hall co-efficient, carrier mobility, carrier concentration, mean free path and mean free time were also studied. These results suggest that the investigated films are semiconducting in nature.

3.5 Bedoya-Hincapié et. al (2014) studied the "Structural and morphological behavior of bismuth thin films grown through DC-magnetron sputtering". Bismuth thin films were grown onto glass substrates through the DC magnetron sputtering technique. The effects of substrate temperature on the microstructure of the films were evaluated. The structural behavior was analyzed via X-ray diffraction, and it showed a marked influence of the substrate temperature on the crystallite size and the micro-stress. The morphologies evaluated through Electron Probe Microanalyzer images indicated a slight difference in the grain size with an increase in temperature as well as a significant increase in surface roughness, according to profilometer measurements.

3.6 Osterhage et. al (2014) studied the "thermoelectric properties of topological insulators Bi_2Te_3, Sb_2Te_3 and Bi_2Se_3 thin film quantum wells". The thermoelectric (TE) figure of merit *ZT* of topological insulator Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3 thin film quantum wells is calculated for thicknesses below 10 nm, for which hybridization of the surface states as well as quantum confinement in the bulk are individually predicted to enhance *ZT*. Here, the question is addressed what *ZT* can be expected from coexisting surface and bulk states in such quantum wells. It is demonstrated that the parallel contributing bulk and surface channels tend to cancel each other out. This is because the surface-to-volume ratios of the thin films prevent the domination of transport through a single channel and because the individual bulk and surface *ZT*s are optimized at different Fermi levels.

3.7 Mahesh et. al (2014) studied the "Temperature Dependent Optical and Morphological Properties of Sb_2Te_3 Thin Films". Sb_2Te_3 thin films at different temperature ranging from room temperature to 200°C were prepared on glass substrate by thermal evaporation method. The effects of temperature on optical and morphological properties of thin films were studied. AFM images indicated crystalline nature of Sb_2Te_3. The optical properties exhibited a decreasing trend of band gap from 1.24eV to 1.06eV with increase in temperature. Transmittance decreased as the temperature was increased and thin film displayed no transmittance in the visible range at 200°C. Surface roughness decreased up to 150°C after which it increased. The surface roughness increased as observed by AFM measurement. On the basis of these properties, the authors observed that Sb_2Te_3 thin films can be used in photovoltaic applications.

3.8 Min Lin et. al (2013) studied the "Annealing effect on the thermoelectric properties of Bi_2Te_3 thin films prepared by thermal evaporation method". Bismuth telluride-based compounds are known to be the best thermoelectric materials within room temperature region, which exhibit potential applications in cooling and power generation. In this paper, thermal evaporation processes were adopted to fabricate the n-type Bi_2Te_3 thin films on SiO_2 /Si substrates. The influence of thermal annealing on the microstructures and thermoelectric properties of Bi_2Te_3 thin films was investigated in temperature range 100-250°C. The crystalline structures and morphologies were characterized by X-ray diffraction and field emission scanning electron microscope analyses. The Seebeck coefficients, electrical conductivity, and power factor were measured at room temperature. The experimental results showed that both the Seebeck coefficient and power factor were enhanced as the annealing temperature was increased. When the annealing temperature was kept at 250°C for 30 min, the Seebeck coefficient and power factor of n-type Bi_2Te_3 -based thin films were found to be about -132.02 μV/K and 6.05 μW/cmċK2, respectively.

3.9 Wang et. al (2012) studied the "The Coexistence of Superconductivity and Topological Order in the Bi_2Se_3 Thin Films". Three-dimensional topological insulators (TIs) are characterized by their nontrivial surface states, in which electrons have their spin locked at a right angle to their momentum under the protection of time-reversal symmetry. The topologically ordered phase in TIs does not break any symmetry. The interplay between topological order and symmetry breaking, such as that observed in superconductivity, can lead to new quantum phenomena and devices. The authors fabricated a superconducting TI/superconductor heterostructure by growing dibismuth triselenide (Bi_2Se_3) thin films on superconductor niobium diselenide substrate. Using scanning tunneling microscopy and angle-resolved photoemission spectroscopy, they observed the superconducting gap at the Bi_2Se_3 surface in the regime of Bi_2Se_3 film thickness where topological surface states form. This observation lays the groundwork for experimentally realizing Majorana fermions in condensed matter physics.

3.10 Gonclaves et. al (2011) studied the "thermal co-evaporation of Sb_2Te_3 thin film optimized for thermoelectric application". Antimony telluride (Sb_2Te_3) is a chalcogenide material used in thermoelectric applications. The deposition of thin films of Sb_2Te_3 requires a precisely controlled process to achieve a desirable high thermoelectric figure-of-merit. The optimization of the thermal co-evaporation process for p-type Sb_2Te_3 thin-film onto plastic substrates for thermoelectric applications is reported. The influence of deposition parameters and composition on thermoelectric properties was studied, seeking optimal thermoelectric performance. Energy-dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy all confirmed the formation of Sb_2Te_3 thin films. Seebeck coefficient (up to 190 μVK^{-1}), in-plane electrical resistivity (8–15 μΩm), carrier concentration (1×10^{19}–7×10^{19} cm^{-3}) and Hall mobility (120–180 $cm^2V^{-1}s^{-1}$) were measured at room temperature for the best of Sb_2Te_3 thin-films.

3.11 Liang He et. al (2011) studied the "Epitaxial growth of Bi_2Se_3 topological insulator thin films on Si (111)". They reported the epitaxial growth of Bi_2Se_3 thin films on Si (111) substrate, using molecular beam epitaxy (MBE). They showed that the as-grown samples have good crystalline quality, and their surfaces exhibit terrace like quintuple layers. Angel-resolved photoemission experiments demonstrate single-Dirac-cone like surface states. These results

combined with the temperature- and thickness-dependent magneto-transport measurements, suggest the presence of a shallow impurity band. Below a critical temperature of ~100K, the surface states of a 7 nm thick film contribute up to 50% of the total conduction. In our ultra-thin Bi_2Se_3 MBE grown thin films, the successful demonstration of the dominating surface states in magneto transport measurements, provides a first but yet important step toward the fabrication of multifunctional heterostructures for innovative nanoelectronics and spintronics.

3.11 **Yi Zhang et. al (2010)** studied the "Doping effects of Sb and Pb in epitaxial topological insulator Bi_2Se_3 thin films: An *in situ* angle-resolved photoemission spectroscopy study". Bi_2Se_3 is a typical three-dimensional topological insulator but always exhibits metallic behavior due to heavy n-type doping. With *in situ* angle-resolved photoemission spectroscopy, the authors systematically studied the doping effects of Sb and Pb on the electronic structure of Bi_2Se_3 films prepared by molecular beam epitaxy method. The surface chemical potential of Bi_2Se3 can be tuned to 110 and 145 meV by doping with Sb and Pb atoms, respectively. By co-doping with Pb and Sb, the Fermi level can be shifted from above to below the Dirac point. The underlying mechanism in different doping effects of Sb and Pb is discussed.

3.12 **Goncalves et. Al (2010)** studied the "Optimization of thermoelectric properties on Bi2Te3 thin films deposited by thermal co-evaporation". The optimization of the thermal co-evaporation deposition process for n-type bismuth telluride (Bi2Te3) thin films onto polyimide substrates for thermoelectric applications is reported. The influence of deposition parameters (evaporation rate and substrate temperature) on film composition and thermoelectric properties was studied for optimal thermoelectric performance. Energy-dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy investigations confirmed the formation of Bi2Te3 thin films. Seebeck coefficient (up to 250 μVK^{-1}), in-plane electrical resistivity (≈10 μΩm), carrier concentration (3×10^{19} - 20×10^{19} cm^{-3}) and Hall mobility (80 - 170 $cm^2\ V^{-1}\ s^{-1}$) were measured at room temperature in selected Bi_2Te_3 samples.

3.13 **Pradyumnan et. al (2009)** studied the "Thermoelectric properties of Bi_2Te_3 and Sb_2Te_3 and its bilayer thin films". The Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3-Sb_2Te_3 bilayer thin films of various thickness have been prepared using thermal evaporation at vacuum. X-Ray diffraction method is used for the characterization of the samples. Electrical studies have been carried out using the standard four probe method and then the activation energies of each film before and after annealing are obtained. Thermoelectric behaviour of each sample is also determined in various temperature regions.

3.14 **Haijun Zhang et. al (2008)** studied the "Topological insulators in Bi_2Se_3, $Bi_2Te_3$and Sb_2Te_3 with a single Dirac cone on the surface". Topological insulators are new states of quantum matter in which surface states residing in the bulk insulating gap of such systems are protected by time-reversal symmetry. The study of such states was originally inspired by the robustness to scattering of conducting edge states in quantum Hall systems. Such analogies have resulted in the discovery of topologically protected states in two-dimensional and three-dimensional band insulators with large spin–orbit coupling. The only known three-dimensional topological insulator Bi_xSb_{1-x}, which is an alloy with complex surface states. The authors present in the article the results of first-principles electronic structure calculations of the layered, stoichiometric crystals Sb_2Te_3, Sb_2Se_3, Bi_2Te_3 and Bi_2Se_3. Their calculations predict that Sb_2Te_3, Bi_2Te_3 and Bi_2Se_3 are topological

insulators, whereas Sb_2Se_3 is not. These topological insulators have robust and simple surface states consisting of a single Dirac cone at the Γ point. In addition, they predict that Bi_2Se_3 has a topologically non-trivial energy gap of 0.3 eV, which is larger than the energy scale of room temperature. They further present a simple and unified continuum model that captures the salient topological features of this class of materials.

3.15 **Youngkun Ahn (2007)** studied the Bismuth thin films prepared by thermal evaporation method. Thin films of bismuth with different thicknesses were fabricated by thermal evaporation method onto cleaned silicon (100) substrates and fused glass at room temperature under ultra-high vacuum condition. The thin films were characterized by using AFM, XRR, XRD and four-point probe method. As a result, around the 15 ~18 nm film thickness, significant changes were observed in the surface morphology, topography, density and resistivity for thin films of thickness from 15 to 18 nm. The grain shape in the films was also changed from spherical to polyhedron-shape and surface RMS roughness was increased significantly around that thickness. The density of bismuth layer of the films shows drastic change, it was raised dramatically as thickness was increased and began to saturate at its bulk density. On the basis of resistivity, bismuth thin films were divided into two groups, one which had high values of resistivity while the other which showed relatively low values of resistivity at the same thickness. The initial growth conditions of bismuth thin film deposited by thermal evaporation method were also investigated by him by using XRR and XPS study. It was observed that there is a bismuth oxide layer between silicon substrate and pure bismuth layer interface, which increases the resistivity of the film. The thickness of the bismuth oxide layer was found to be maintained at about 3 nm.

3.16 **Gonclaves et. al (2006)** studied the "Thermoelectric Properties of Bi_2Te_3/Sb_2Te_3 Thin Films". The deposition and characterization of n-type Bi_2Te_3 and p-type Sb_2Te_3 semiconductor films are reported. The films were deposited by thermal co-evaporation on a 25 μm thick substrate. The co-evaporation method is inexpensive, simple, and reliable, when compared to other techniques that need longer time periods to prepare the starting material or require more complicated and expensive deposition equipment. Seebeck coefficients of -189 μVK^{-1} and +140 μVK^{-1} and electrical resistivities of 7.7 μOhm and 15.1 μOhm were measured at room temperature on n-type and p-type films, respectively. These values are better than those reported for films deposited by co-sputtering or electrochemical deposition, and are close to those reported for films deposited by metal-organic chemical vapour deposition or flash evaporation. Because of their high figures of merit, these films can be used for the fabrication of a micro-Peltier element, useful in temperature control and laser-cooling for telecommunications.

3.17 **Sean Echols et. Al (2002)** studied the "Thermal evaporative growth of high-quality bismuth thin films". In an attempt to create high quality bismuth thin films, they had developed a technique for producing large bismuth grains. A thin layer of germanium (~200 angstroms) was grown on glass substrates (both at room temperature and heated to 150 °C), followed by the evaporation of the bismuth thin film (~10 μm). The substrates were then individually placed in a tube furnace and annealed in an N_2 environment at various temperatures, both above and below the melting point of bismuth. The films were characterized through direct current resistance and magnetoresistance measurements. Although the quality of the films produced was not comparable with films created by other methods, they believed that further investigation will yield higher quality films. According to the authors, this research made provided much insight into the nature of bismuth and bismuth thin films, and made suggestions for further experimentation.

4. Research Gaps:

As mentioned above, thin films of Bi, Te, Sb and Bi_2Te_3 and Sb_2Te_3 topological insulators have been investigated earlier by some authors but effective comparison of their properties with that of topological insulator phase is not available in literature. As such a systematic study of thin films of these materials with comparison of their properties with topological insulator phase may further enrich our knowledge about these materials.

5. MOTIVATION

Topological insulators are fascinating materials. they are insulators as well as semiconductors. They have spin dependent conducting states. They show integral quantum hall effect and quantum spin hall effect. They have vast applications in thermoelectric materials, photo detector, magnetic devices, field-effect transistor, laser, medicine etc. Inspired by these properties of topological insulators, I thought to investigate thin films of Bi, Sb, Te and their binary mixtures vis a vis their topological insulator phase to check for their structural, electronic and optical properties.

6. OBJECTIVES

1. To prepare thin films of Bi, Te and Sb (any two) metals and their binary mixtures on glass or silicon substrate by using thermal evaporation method.
2. To characterize the thin films by using XRD, TEM, AFM, XPS and UV-Vis spectroscopy.
3. To prepare thin film of topological insulator Bi_2Te_3 or Sb_2Te_3 (as the case may be) on glass/silicon substrate and compare its properties with those of other binary mixture thin films of these materials.
4. To theoretically investigate electronic structure of these materials i.e., Bi, Te and Sb (any two) metals, their binary mixtures and their topological insulator phase, viz., Sb_2Te_3 or Bi_2Te_3.

7. RESEARCH METHODOLOGY

There are various types of thin film deposition techniques, which are as follows:

1. Thermal evaporation method
2. Sputtering method
3. Sol-gel method
4. Chemical bath deposition method

In the present study we propose to use thermal evaporation method for preparing thin films.

7.1 Thermal Evaporation Method

A typical thermal evaporation system is schematically shown in figure. The system consists of an evaporation source that vaporizes the desired material and a substrate is located at an appropriate distance facing the evaporation source. Both the source and the substrate are located in a vacuum chamber. The substrate can be heated or electrically biased or rotated during deposition. The desired vapor pressure of source material can be generated by simply heating the source to elevated temperatures, and the concentration of the growth species in the gas phase can be easily controlled by varying the source temperature. The substrate temperature during the thin film deposition is measured using chromel-alumel thermocouple kept in good thermal contact with the substrate. The rate of deposition and thicknesses of the films are continuously monitored during the film deposition using a quartz crystal thickness monitor DTM -101 (Hind Hi Vac., India). In order to improve crystallinity, the evaporated thin films are deposited at different substrate temperatures (Ts).

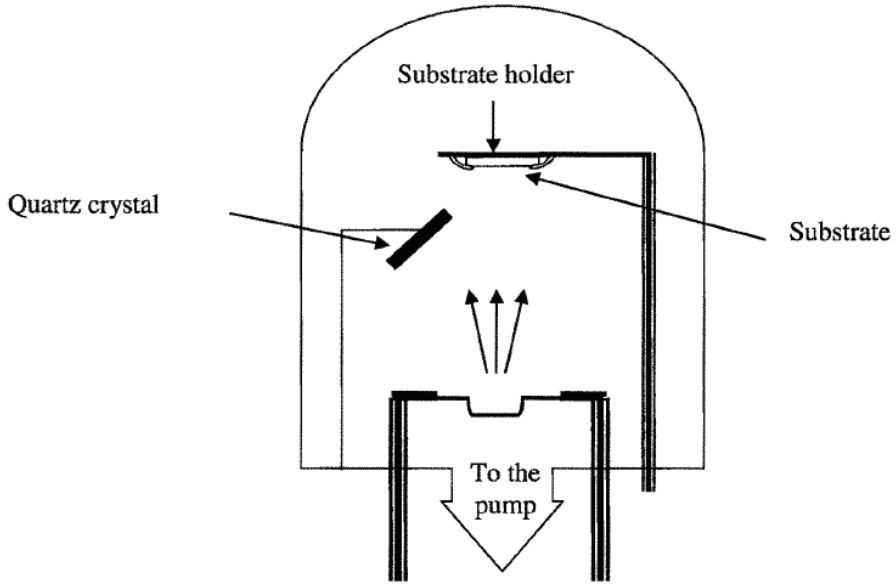


Fig 1. A schematic of the thermal evaporation system.

7.2 Thin film characterization techniques

7.2.1 X-Ray Diffraction method (XRD)

X-ray diffraction (XRD) is a very powerful experimental technique for studying crystal structures of solids and thin films. The preferred orientation of crystallites grown in semiconducting thin-film samples obtained from XRD analysis.

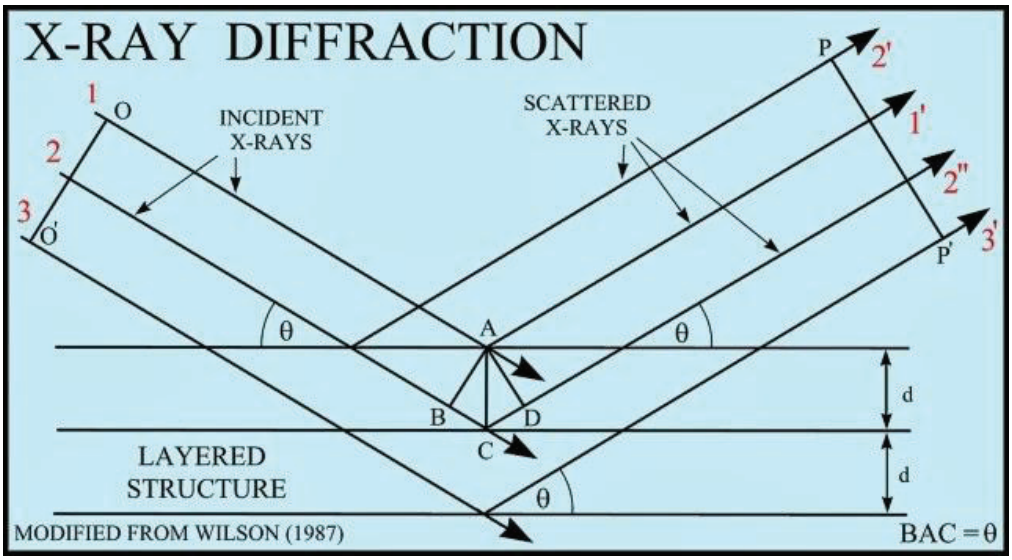


Fig. 2: schematics of X-Ray diffraction

In XRD analysis, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to **2 Å,** is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law:

$$2d\sin\Theta = n\lambda$$

where d is the spacing between atomic planes in the crystalline phase and ʎ is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle Θ. This diffraction pattern is used to identify the crystalline phases present in thin films.

The crystallite size, d, can be estimated from the peak width in XRD pattern by using the Scherrer's formula : d = *K*ʎ BcosG

where ʎ is the X-ray wavelength (ʎ = 0.15418 nm with Cu Ka radiation) B is the full width at half maximum (FWHM) of a diffraction peak, Θ is the diffraction angle, and K is the Scherrer's constant of the order of unity for usual crystal and thin films. It is important to note that X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizable amount of powder and thickness of thin films.

7.2.2 Scanning Electron Microscope (SEM)

The morphological and compositional characterization of the semiconducting thin films in this work are carried out using scanning electron microscope ESEM.

A schematic representation of a typical SEM is shown in figure 3.

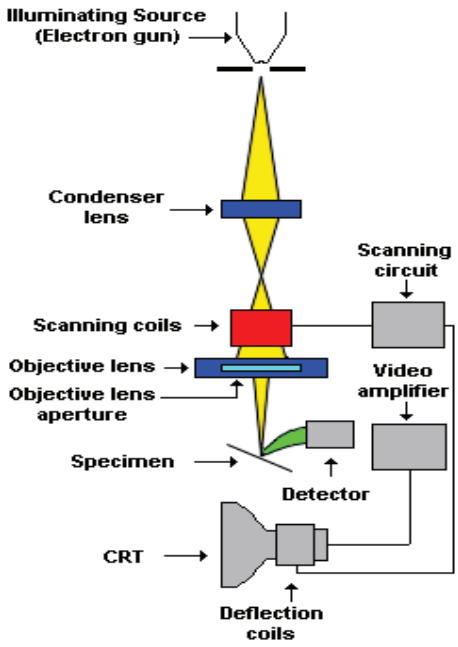


Fig. 3. Schematic of scanning electron microscope

Electrons emitted from an electron gun pass through a series of lenses to be focused and scanned across the sample. Electron beams having energies ranging from 0.5 keV to 30 keV, are focused by one or two condenser lenses. The beam then passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens.

When the electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen

current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a cathode ray tube (CRT). The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image can be digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

7.2.3 Transmission electron microscope (TEM)

Transmission electron microscope (TEM) is, in principle, similar to optical microscopes; both contain a series of lenses to magnify the surface of the test sample. Transmission electron microscopy was originally used for higher magnification. Later, analytical capabilities such as electron energy loss detectors and X-ray detectors are also added to the instrument and the technique is now also known as either “microscopy” or “microscope.”

A schematic of a transmission electron microscope is shown in figure 4.

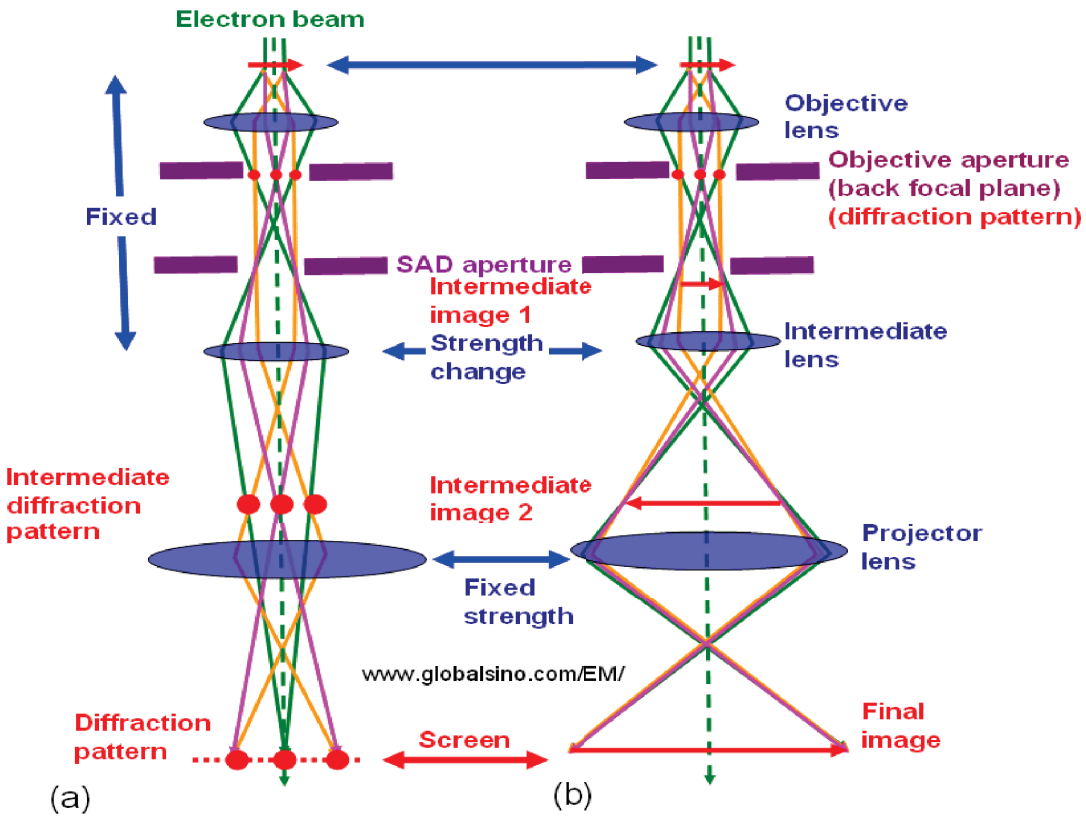


Fig. 4: schematics of TEM

Electrons from an electron gun are accelerated to high voltages and focused on the sample by the condenser lenses. The sample is placed on a small copper grid, a few mm in diameter. The static beam has a diameter of a few microns. The sample must be sufficiently thin (a few tens to a few hundred nm) to be transparent to electrons. The transmitted and forward scattered electrons
form a diffraction pattern in the back focal plane and a magnified image in the image plane.
With additional lenses, either the image or the diffraction pattern is projected onto a fluorescent screen for viewing or electronic or photographic recording. The ability to form a diffraction pattern yields structural information.
Selected area (electron) diffraction (abbreviated as SAD or SAED), is a crystallographic experimental technique that can be performed inside a transmission electron microscope (TEM). To obtain SAD pattern the wavelength of high-energy electrons is incident on very thin,(-50-100 nm), semiconducting film is kept. The atoms in the film act as a diffraction grating to the electrons, which are diffracted. That is, some fraction of them will be scattered to particular angles, determined by the crystal structure of the sample, while others continue to pass through the sample without deflection. As a result, the image on the screen of the TEM will be a series of spots known as the selected area diffraction pattern. Here, each spot corresponds to a satisfied diffraction condition of the sample's crystal structure.

7.2.4 Atomic Force Microscope (AFM)

Atomic force microscope is a versatile tool to investigate the morphology and growth structure of the thin films.
The operating principle of AFM is illustrated in figure. The instrument consists of a cantilever with a sharp tip mounted on its one end. The cantilever is usually formed from silicon, silicon oxide or silicon nitride and is typically 100 pm long, 20 pm wide, and 0.1 pm thick. The vertical sensitivity of cantilever

depends on its length, which can be sensed by one or several methods . The cantilever motion causes the reflected light to impinge on different segments of the photodiode.

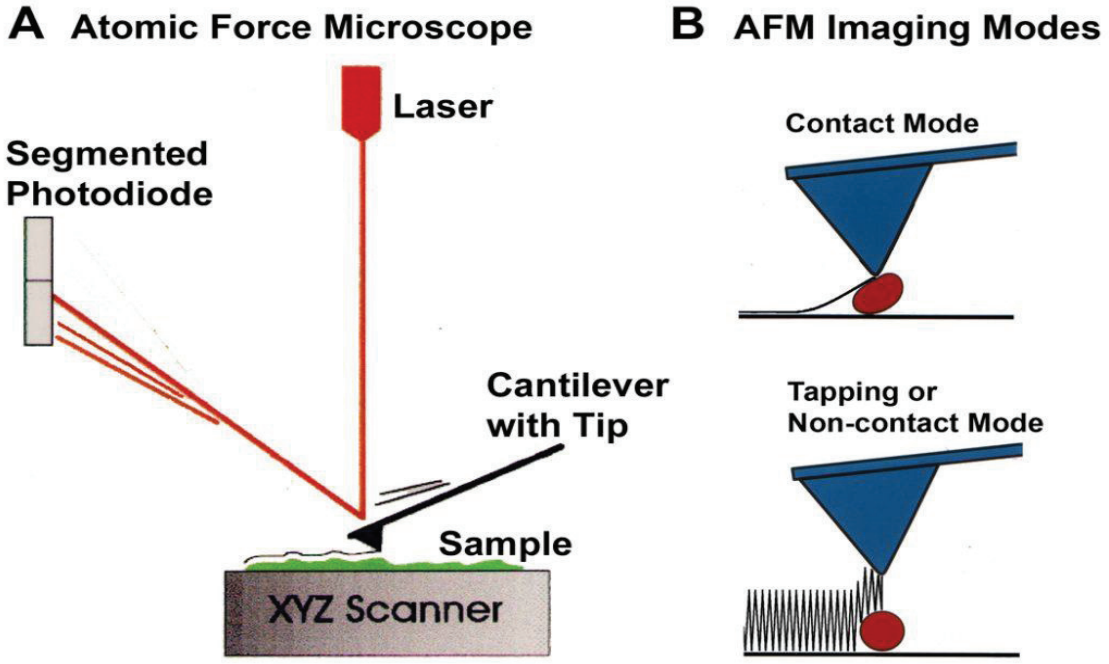


Fig.5: schematics of AFM; (A) AFM, (B) imaging modes

Cantilevers come in two common shapes as shown in figure 2.8. The three common modes of operation of AFMs are, 1) Contact mode, 2) Non- contact mode, and 3) Tapping mode.

In the contact mode, the probe tip is dragged across the surface and the resulting image is a topographical map of the sample surface. The dragging motion of
forces are substantially weaker than the contact mode forces, so weak in the probe lip, combined with adhesive forces between the tip and the surface can distort measurement data and damage the sample. In the non-contact mode, the instrument senses Van-der Waal attractive forces between the surface and the probe tip held above the sample surface.
Non-contact mode provides lower resolution than either contact or tapping mode. Tapping mode imaging overcomes the limitations of the conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface are also in use. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50 to 500 kHz. Tapping mode imaging works well for soft, adhesive, or fragile samples, allowing high resolution topographic imaging of sample surfaces that are easily damaged or otherwise difficult to image by other AFM techniques.

7.2.5 Four point probe method

The four-point probe is commonly used technique to measure the semiconductor resistivity. It is an absolute measurement without recourse to calibrated standards and is sometimes used to provide standards for other resistivity measurements. The schematic diagram of four-point probe measurement technique is shown in figure 6. It is seen that by applying current between terminal 1 and 4 (outer terminals in the figure) and measuring voltage V across terminal 2 and 3 (inner terminals) one can calculate sheet resistance (R_{sh}) of the film using the following equation.

$$R_{sh} = \frac{\pi}{\ln 2}\left(\frac{V}{I}\right)$$

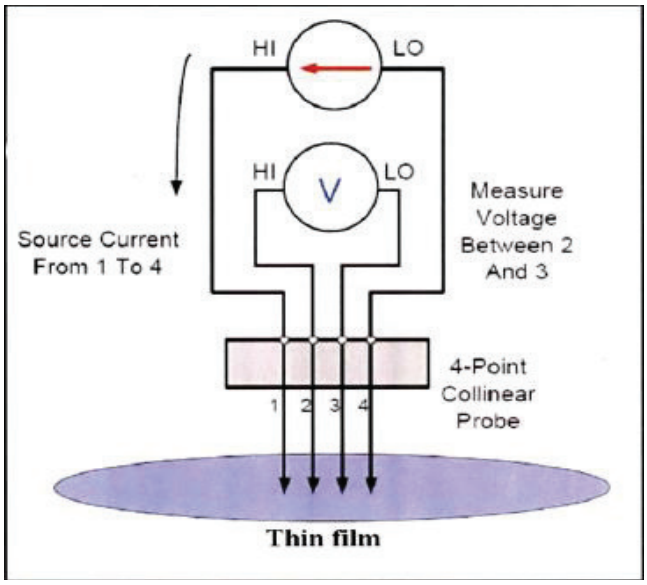


Fig. 6: four point probe method for resistivity measurement

7.2.6 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray Photoelectron Spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA) is the most widely used surface analysis technique because it can be applied to a broad range of materials and provides valuable quantitative and chemical state information from the surface of the material being studied. The average depth of analysis for an XPS measurement is approximately 5 nm. PHI XPS instruments provide the ability to obtain spectra with a lateral spatial resolution as small as 7.5 µm. Spatial distribution information can be obtained by scanning the micro focused x-ray beam across the sample surface. Depth distribution information can be obtained by combining XPS measurements with ion milling (sputtering) to characterize thin film structures. The information XPS provides about surface layers or thin film structures is important for many industrial and research applications where surface or thin film composition plays a critical role in performance including: nanomaterials, photovoltaics, catalysis, corrosion, adhesion, electronic devices and packaging, magnetic media, display technology, surface treatments, and thin film coatings used for numerous applications.

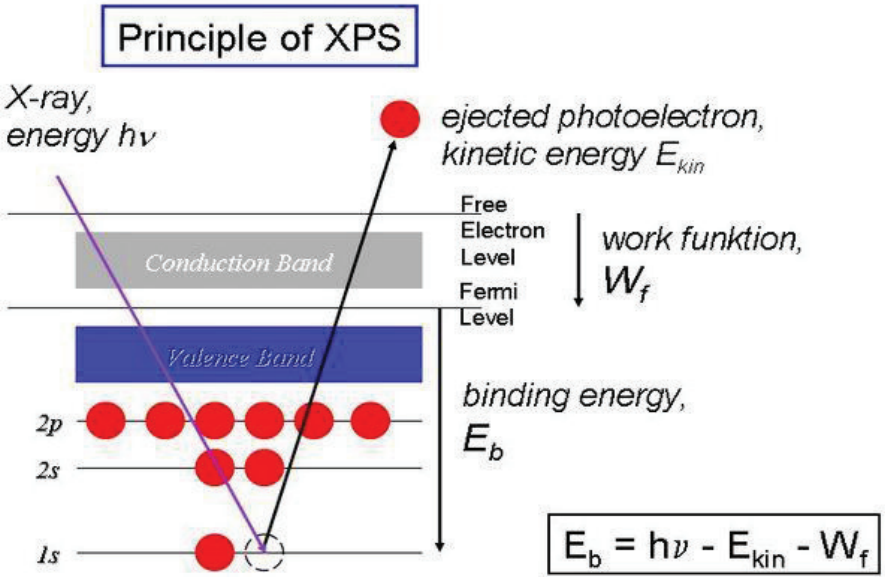


Fig. 7: schematics of XPS

XPS is typically accomplished by exciting a sample's surface with mono-energetic Al k_α x-rays, causing photoelectrons to be emitted from the sample surface. An electron energy analyzer is used to measure the energy of the emitted photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined.

Physical Electronics XPS instruments function in a manner analogous to SEM/EDS instruments that use a finely focused electron beam to create SEM images for sample viewing and point spectra or images for compositional analysis. With the PHI XPS instruments, a finely focused x-ray beam is scanned to create secondary electron images for sample viewing and point spectra or images for compositional analysis. The size of the x-ray beam can be increased to support the efficient analysis of larger samples with homogeneous composition. In contrast to SEM/EDS which has a typical analysis depth of 1-3 µm, XPS is a surface analysis technique with a typical analysis depth of less than 5 nm and is therefore better suited for the compositional analysis of ultra-thin layers and thin micro scale sample features.

7.2.7 UV Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectra region. This means it uses light in the visible and adjacent ranges. The absorption and reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.
Molecules containing pie-electrons or non-bonding electrons (n electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb.
UV-Vis spectroscopy is used in the semiconductor industry to measure the thickness and optical properties of thin films. UV-Vis spectrometers are used to measure the reflectance of light.

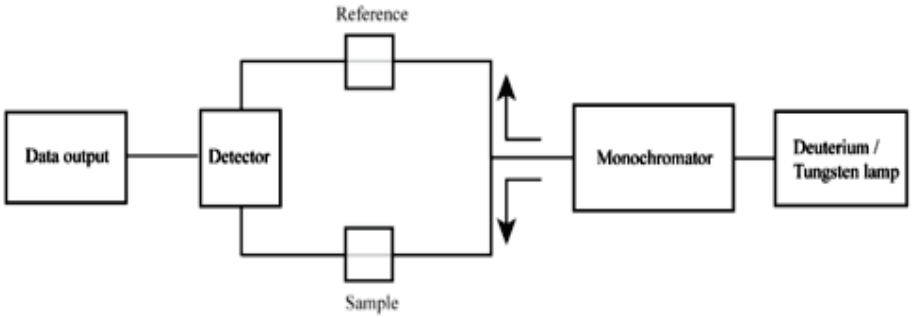


Fig. UV-Vis spectroscopy

Reserch Work Plan

- First three months we will do literature survey and learn the operation of thermal evaporation unit for making thin films. Meanwhile we will procure the required samples also.
- Next three months we will deposit thin films of Bi, Te and their binary mixtures and investigate the films.
- Next three months we will deposit thin film of Bi_2Te_3 topological insulator and investigate the same for making comparison of their properties with Bi-Te binary thin films and writing research papers.
- Next three months we will prepare thin films of Sb, Te and their binary mixtures and topological insulator Sb_2Te_3 and investigate them for comparing their properties and writing research paper.
- After that next three months we will theoretically investigate the electronic structure of Bi, Te and Sb (any Two) metals and their binary mixture Bi_2Te_3 or Sb_2Te_3 .
- We will give next six months for writing of thesis.

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